



The synergistic effect between supercritical water and redox properties of iron oxide nanoparticles during in-situ catalytic upgrading of heavy oil with formic acid. *Isotopic study*

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ARTICLE INFO

Keywords:

Heavy oil
Upgrading
Iron oxide nanoparticles
Isotopic analysis
Supercritical water

ABSTRACT

Catalytic treatment in water medium under high-pressure condition could be an attractive technology for clean upgrading of heavy crude oils and residua with effective heteroatom removal to meet the qualified liquid transportation fuels. By applying isotope labeling technique, an experimental study has been reported here to gain insights in the catalytic performance of iron/iron oxide nanocatalysts for upgrading vacuum residue (VR) in supercritical water (SCW) and formic acid (FA) solution. The results show that the hematite iron oxide nanoparticles with a higher oxidation state (Fe^{3+}) are more effective in the oxidative removal of heteroatoms (sulfur, nitrogen) and in the reduction of heavy constituents (e.g., asphaltene) to light oil; while, magnetite ($\text{Fe}^{3+}/\text{Fe}^{2+}$) is superior in the hydrogenation of light hydrocarbons. Contrary to the upgrading in the steam atmosphere, SCW has strong influence on the recovery of converted iron oxide to the higher oxidation state ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$), which can recompense the lattice oxygen loss of the catalyst during the cracking process. The advantage of heavy oil upgrading by using iron oxide nanoparticles in SCW + FA solution is that water pressure can enhance the capability of catalyst in providing the oxygen for the oxidative cracking as well as the effective hydrogenation of heavy oil by active hydrogen from the water-gas shift reaction.

1. Introduction

Although there are serious concerns about the environmental consequences of the fossil fuels, it has still sustained about 80% of the global demands [1]. Since the world energy consumption rises continually, there have been indispensable efforts to compensate the depleted global light oil reserves by utilizing the unconventional heavy oils like bitumen and residua. [2,3]. However, there is a big challenge in using these heavy oils due to their inherent properties i.e. high density (low API gravity), high viscosity, low hydrogen content, the presence of high molecular weight compounds (resins and asphaltenes), high contents of the hetero atoms (nitrogen, sulfur and oxygen) and metals, particularly nickel and vanadium [4]. These feeds can cause common problems in cracking process, such as low yields of light fractions and catalyst deactivation, mainly due to metal deposits and coke formation, which represent a great challenge for further processing stages [4]. In addition, removal of sulfur-containing compounds from the heavy crudes becomes very important due to their high

contents of sulfur and mounting environmental concerns associated with SO_x emissions [4].

Generally, the upgrading technologies of crude heavy oils (e.g. bitumen) and residua (atmospheric or vacuum bottom) can be divided into two main categories [4,5]: The carbon rejection technologies, the thermal processes with low-qualified upgraded oil products, that are technically simpler than the second type processes, namely the processes of adding hydrogen, specified with the upgrading of heavy oil in the presence of hydrogen. The latter, hydrogen addition processes, are known as catalytic processes with the advantages of high-qualified light oil product with smaller amounts of coke against non-catalytic thermal processes. However, the addition of gaseous hydrogen from external source can impose some environmental challenges, since hydrogen is supplied from methane reforming process [4]. Although the hydrogen donor solvents with a great impact on the coke suppression [6–10] have been proposed as an alternative for the hydrogenation of heavy oil vacuum residue (VR)

In some studies, the use of catalysts such as metal/metal oxides

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Table 1
Physico-chemical properties of vacuum residue feed used in this research.

Physical Properties ^a				Content ^b		Elemental analysis (wt %) ^c						
API Gravity ^{20°C}	M _w	SG ^{20°C}	ν ^{80°C}	maltene (SAR)	aspheltene	C	H	S	N	O	Cl	Ash (wt%)
8.90	(g/mol) 1860	(g/cm ³) 1.008	(mm ² /s) 2550	(wt %) 79	(wt %) 21	82.06	9.19	3.92	0.72	2.35	0.47	1.31

^a M_w: molecular weight of VR feed, SG²⁰: specific gravity of VR at T = 20 °C, and ν⁸⁰ = kinematic viscosity of VR at T = 80 °C.

^b Separation of maltene (SAR: Saturates, Aromatics, Resins) or n-hexane-soluble fraction from aspheltene (toluene-soluble fraction) was accomplished by solvent extraction technique.

^c Estimated by CHNOS analysis.

[11–16], metal supported on ZSM-5[17,18] and the nanoparticles supported on bacteria [19] have been suggested for upgrading heavy oils, while they can produce high-quality light fuels with less coke formation. Among the catalysts, iron oxide has the advantage of being relatively inexpensive, with a proper stability, nontoxicity, environmental benign, and the ease of surface and/or structural modifications. Fumoto et al. [20] and Funai et al. [14] have examined the durability of hematite (α-Fe₂O₃) catalyst for continuous decomposition of petroleum residue in steam atmosphere. Although the quality of upgraded light oil and the suppression in coke yield were notable, the catalytic activity of iron oxide decreased rapidly in the steam atmosphere. They concluded that the catalyst deactivation occurred by continuous consumption of the lattice oxygen in the hematite structure, and the atmospheric steam was not able to refill the oxygen rapidly.

Recently, the decomposition and upgrading of heavy oil by using high-temperature and high-pressure water has attracted the attention of many researchers [21,22]. The use of water in the hydrothermal and supercritical conditions has proved some promising results as well as presenting an interesting alternative for heavy oil processing. In SC conditions, the physico-chemical properties of water are improved because of enhancement of oil solubility and reduction of oil viscosity in water, which would facilitates the upgrading process [21]. The physical properties (solvation and dispersion) of supercritical water (SCW) can influence the miscibility of oil and water by dissolving the organic molecules to form a uniform phase as well as the capability to suppress the coke deposition on catalyst surface [23]. Contrary to supercritical CO₂ medium [24], in the presence of appropriate catalyst, SCW cooperates as a reactant (e.g., hydrogen donor) in the upgrading process as a highly efficient conversion technique [25–28]. In our previous studies [29,30], the oxidative catalytic cracking of heavy oil in SCW over hematite nanoparticles demonstrated the active role of both the lattice oxygen from catalyst and active hydrogen from the water on cracking of the heavy oil in SCW. In the presence of CO, CO₂, H₂, and H₂O, active hydrogen (AH) is defined as the hydrogen produced via the water-gas shift reaction (WGS: CO + H₂O → H₂ (AH) + CO₂) [31–34] and reverse water gas shift reactions (RWGS: CO₂ + H₂ + H₂O → CO + 2H₂O → 2H₂ (AH) + O₂) [35], which is an effective method for the hydrogenation of heavy oil and the model compounds. However, without catalyst, the amount of AH from water is not adequate to moderate the population of free radicals formed during the heavy oil processing in SCW.

The present paper proposes the oxidative cracking of VR with iron oxide in the presence of formic acid (FA) and SCW solution (FA + SCW). Formic acid, as a compound, which can be recovered from renewable sources [36], is a proper candidate as hydrogen-donor compound. In SCW, it decomposes to CO, CO₂, and H₂ via dehydration and decarboxylation paths (H₂ + CO₂ ← HCOOH → CO + H₂O), that can provide an effective method for hydrogenation of heavy oils with the strong suppression in coke formation [37]. Due to the positive effect of iron oxide as catalyst of WGS, more AH can be provided in the presence of iron oxide. In addition, the removal of heteroatoms with a series of hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodemetallization (HDM) reactions, is expected to be accelerated during heavy oil upgrading in SCW. Due to the strict environmental

regulations on transporting fuels, this can be indeed advantageous.

To study the synergistic effect of SCW and iron oxide during the heavy oil upgrading in the presence of FA, firstly, the oxidative state of iron with different valences (Fe⁰ of iron, Fe²⁺/Fe³⁺ of magnetite, or Fe³⁺ of hematite) should be understood after its treatment in SCW and FA + SCW. Study of this matter is beneficial due to the oxidative nature of the cracking system which consumes the lattice oxygens from iron oxide. Thereafter, the contribution of water as the hydrogen donor via WGS-RWGS reaction during VR upgrading has been traced by replacing H₂O with D₂O (isotope labeling). This contribution reveals the positive effect of water pressure on the redox capability (Fe³⁺ ↔ Fe²⁺) of iron with supporting of the catalyst against the lattice oxygen depletion and the deactivation of catalyst which is observed in the atmospheric steam condition.

2. Experimental section

2.1. Materials

Vacuum residue, VR, with initial boiling point of > 550 °C recovered from the bottom of the vacuum distillation tower at Tehran Refinery, Iran. The elemental analysis and the chemical composition along with other properties (molecular weight, density, and viscosity) of VR are shown in Table 1. Toluene (99%), n-hexane (99.6%), chloroform (99%) and formic acid (98%) were purchased from Merck chemical company. Deuterium oxide (99.9 atom% D) has been prepared by Sigma–Aldrich. All chemicals were used as received. Moreover, the deionized water prepared in-house has been used throughout the experiments. Magnetite (Fe³⁺/Fe²⁺) and iron powder (Fe⁰) were purchased from Sigma–Aldrich with the particle size in the range of 50–100 nm and < 10 μm, respectively. Hematite (Fe³⁺) nanoparticles in the same range of magnetite was prepared from iron (III) nitrate under SCW.

2.2. Synthesis of hematite (α-Fe₂O₃) nanoparticles

In order to prepare hematite nanoparticles, SCW synthesis route, with the high capability of controlling the size distribution of synthesized particles was applied. The initial source of iron (III) nitrate hexahydrate (Fe(NO₃)₃·6H₂O) from Merck AG. For synthesis) was used for the hydrothermal synthesis of α-Fe₂O₃ nanoparticles. 0.1 mol/ml³ of Fe (NO₃)₃ aqueous solution (50 ml) was heated in a stainless steel autoclave (200 ml) at 450 °C for 120 min. This operational working condition has been optimized according to the previous studies [38]. Thereafter, the reaction vessel was immediately cooled by water and the precipitates were separated by using high-speed centrifugation. Then the particles were dried on Petri dishes under ambient conditions.

2.3. Treatment of iron/iron oxide in SCW and SCW + FA solution

In order to examine the effect of SCW and SCW + FA on phase transformation of iron with different oxidation state (iron, magnetite, or hematite), as well as the effect of catalyst on the distribution of the gas product (H₂, CO, and CO₂), in the case of FA decomposition in SCW

condition, various experiments have been conducted by a high pressure bomb reactor (10 cm^3), which was equipped with a valve for the gas sampling. The reactor was loaded with FA, water, and catalyst with definite ratio (catalyst: water = 1:20 g/g, FA: water = 1:2 v/v) and prior to the reaction, the air inside the reactor was substituted by nitrogen gas and the valve was closed. Then it was sealed and submerged in a sand bath to heat the system up to a reaction temperature (350, 400, 450, or 500 °C). Heat-up time was around 2 min. After 10 min passed from the reaction, the reactor was taken out of the bath and rapidly cooled in a water bath. Then the reactor was connected to a gas bag to analyze the gas contents by the gas chromatograph (GC). The spent catalyst was also recovered for the observation of the oxidation state of iron after contacting with the only SCW or SCW + FA solution, which appears to be very crucial for the oxidative cracking of heavy oil. For the sake of comparison, the non-catalytic decomposition of FA in SCW, as well as decomposition in nitrogen atmosphere, as the blank tests, have been conducted. Independent test runs have also been replicated under the nominally identical conditions to determine the uncertainties of the experimental results. The reported results of this research represent the mean values for two independent trials.

2.4. Upgrading procedure

As shown in Fig. 1, the feedstock of VR along with water and the catalyst was placed in the stainless-steel batch mini-reactor with 10ml internal volume. The reactor was loaded with feedstocks, water, FA and catalyst with specified ratio (catalyst: water = 1:20 g/g, FA: water = 1:2 v/v and VR: water = 1:2 g/g) and mixture was degassed by purging with N_2 to remove all gas impurities. In a typical run, 1 g of VR, 1 ml of FA, 50mg of catalyst and 2 ml of D_2O were loaded into the reactor, corresponding water density of 0.2 g/ml inside the reactor. Thereafter, the reactor was heated up to the reaction temperature with

the heating time and the reaction time set at 2 and 60 min, respectively. Then the reactor was removed from the heater and it was immersed in ice-water bath for about 30 min to stop the reaction. In the next step, the reactor was opened and the product was recovered using chloroform. Since the produced maltene would contain deuterated compounds, chloroform as a hydrogen-free solvent was used in order to decrease the calculation error of AH_{rel} (see Section 2.5). Chloroform with a low boiling point (compared with toluene) minimizes the loss of light volatile hydrocarbons during vacuum evaporation. Since the exact weight of initial feed (maltene + asphaltene) and the recovered solid product (asphaltene and coke) were measured accurately, the mass balance helped to estimate the weight of maltene. After the removal of chloroform by vacuum evaporation, the product was separated into three fractions, namely maltene, the hexane-soluble fraction comprising saturates, aromatics and resins (SAR), asphaltene (hexane-insoluble/toluene-soluble), and coke (toluene-insoluble). The yield of each fraction (excluded gas fraction) was calculated as the weight percentage of each portion to the total weight of the feed:

$$m_{\text{maltene}} + m_{\text{asphaltene}} + m_{\text{coke}} = m_{\text{feed}} \quad (1)$$

The VR feed contains 79% of maltene and 21% of the asphaltene.

2.5. Characterization of catalyst and oil

The X-ray diffraction (XRD) measurements were conducted at room temperature using a powder diffractometer (Smart Lab; Rigaku Corporation, Tokyo, Japan), with 0.005° step, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). Transmission electron microscopy (JEM-2100; JEOL Ltd., Tokyo, Japan) was used to observe the size and morphology of the particles, and electron diffraction spectroscopy combined with the TEM instrument (TEM-ED) was applied for particle analysis. The elemental abundances of the oil, including carbon, nitrogen, hydrogen, nitrogen

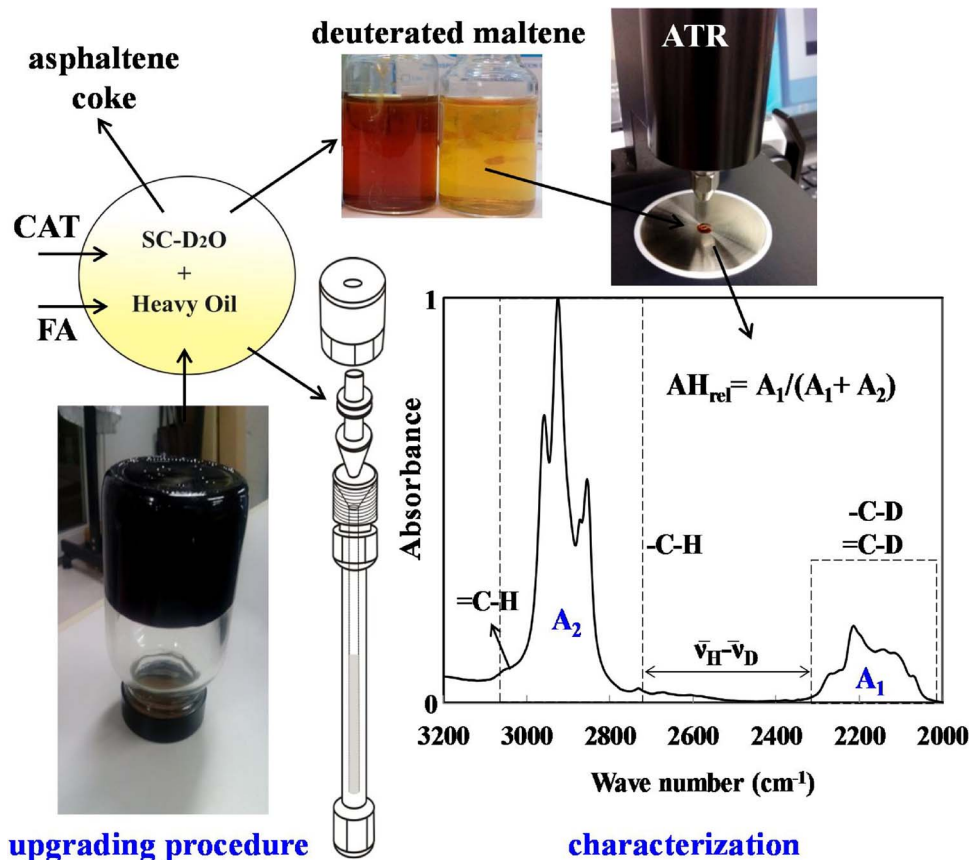


Fig. 1. Experimental procedure of heavy oil upgrading and ATR analysis of deuterated oil to study the contribution of water in hydrogenation of heavy oil.

and sulfur (CHNOS) were measured by an elemental analysis instrument (CHN elements: J-Science company, model JM10, O: Eelementer, Vario Micro Cube and S: Yanaco, model HSU-20). The weight distribution of the upgraded product, as an indicator of the oil volatility/decomposition rate with temperature, was measured by thermogravimetric analysis (TGA) in the argon atmosphere (TMA-50, Shimadzu) in which the sample was heated to 500 °C at a heating rate of 10 K/min and it was kept constant for 5 min. The gas stream (CO, CO₂, and H₂) from decomposition of FA in SCW was analyzed by using a GC which was equipped with thermal conductivity detector (GC-8A, Shimadzu Corp.).

The Infrared (IR) spectroscopy with attenuated total reflectance (ATR) technique has been applied to analyze the deuterated oil product (Cary 630, Agilent, US). Fig. 1 shows the typical spectra of the deuterated sample characterized by this technique. Through defining relative active hydrogen (AH_{rel}) from IR spectra, which is resulted from deuterated oil, a simple and reliable route has been provided to track the participation of water in the hydrogenation via WGS/RWGS paths during the heavy oil upgrading in SCW. The detail of the analysis of deuterated compound by this technique has been explained comprehensively in Appendix A (see Supplementary information).

3. Results and discussion

3.1. Effect of SCW and SCW + FA on the oxidation state of iron/iron oxide

As mentioned before, iron with different valences was treated in the SCW with and without FA. The results of each investigation would provide proper information about SCW and FA on the reduction-oxidation (redox) properties of iron.

3.1.1. Iron (Fe⁰)

Fig. 2(a,b) shows the XRD patterns of the zero valence iron before and after treatment in SCW and SCW + FA, respectively. Obviously, the crystal structure of the iron did not change significantly during SCW treatment in the absence of FA (see Fig. 2a), however, the small peaks of magnetite are appeared at 450 °C and 500 °C, indicating that the crystal structure of iron was hardly changed. Formation of Fe₃O₄ around iron particles in SCW with no FA might prevent further oxidation of iron in short reaction time. On the other hand the magnetite phase is appeared by introducing FA to SCW (Fig. 2b). Furthermore, the intensities of the peaks related to magnetite are increased with increasing temperature. Besides, the analysis of the gas product from the decomposition of FA in SCW, demonstrates a substantial reduction in CO₂ concentration (Fig. 3c), that implies Fe⁰ firstly reacts with CO₂ and H₂O to form FeCO₃, and then undergoes decomposition reaction to form Fe₃O₄:



The overall reaction is oxidation of Fe⁰ to magnetite with evolution of hydrogen to approach to the maximum yield in 350 °C (see Fig. S1 in supplementary):



3.1.2. Magnetite (Fe²⁺/Fe³⁺)

Fig. 2(c) also presents the XRD patterns of the magnetite after its interaction with the lone SCW. It can be seen that contrary to Fe⁰, magnetite is oxidized to hematite easily. The appearance of the peaks related to hematite (Fe³⁺) can be attributed to the water splitting to hydrogen and oxygen over magnetite. The oxygen is stored in the catalyst surface as the lattice oxygen accompanied with hydrogen production, according to the following stoichiometry:



Since this reaction is endothermic ($\Delta H^\circ = +16.3$ kJ/mol), the rising temperature is favorable thermodynamically, hence magnetite conversion to the hematite can be accelerated at higher temperature (see Fig. 2c).

In the presence of FA, however, the peaks related to the hematite phase are intensified (Fig. 2d) up to 400 °C. Regarding the CO and CO₂ concentration in the gas analysis (Fig. 3), it is suggested that the raising temperature shifts the iron to the higher oxidation state; while at the elevated temperatures (T = 500 °C) the backward reaction was accelerated. Consequently, magnetite reaction becomes predominant at 500 °C according to the overall reaction, which is described below:



3.1.3. Hematite (Fe³⁺)

The XRD patterns demonstrates a significant phase change of hematite to the magnetite in the presence of FA, while no phase change has been observed in the presence of the lone SCW (Fig. 2e). Since the reaction of hematite with hydrogen is exothermic ($\Delta H^\circ = -16.3$ kJ/mol), the lower temperature is preferred for the conversion of hematite to magnetite:

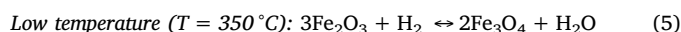


Fig. 2c shows that hematite related peak intensity is increased, indicating that the backward reaction (Eq. 5) in high temperature is thoughtful. Also, the minor change in the phase transition at the higher temperatures could be attributed to the hematite reduction with CO ($\Delta H^\circ = +24.8$ kJ/mol):



These results are in agreement with the results of gas analysis (Fig. 3). By a comparison between the results, it can be concluded that FA in the SCW acts as an oxidant of iron to the higher valences (Fe⁰ → Fe²⁺ → Fe³⁺), and provides a suitable environment for the oxidative cracking of the heavy oil in that environment as well. This issue would be discussed in detail.

The transmission electron microscopy analysis (TEM) has been performed in order to discover the effects of SCW and formic acid solution on the morphology of iron oxide. Compared to the fresh iron oxides (Fig. 4a,c), some agglomerations of nanoparticles have been observed (Fig. 4b,d). This demonstrates that the Ostwald ripening [39] phenomenon has not been stopped completely in SCW, where due to a decline in the dielectric constant of water, the solubility of iron oxide is expected to be suppressed. Apart from the XRD results, electron diffraction analysis of the fresh and the spent catalysts, obtained by TEM, confirm combination of the two phases (hematite and magnetite) after treatment in SCW + FA mixture (see Fig. S2 in supplementary information).

3.2. Catalytic upgrading of VR

In order to examine the chemical effect of water, as the hydrogen donor to the hydrocarbon and oxygen supplier to the catalyst lattice, upgrading of VR in supercritical heavy water (SC-D₂O) has been performed with the different valences of iron in the absence and the presence of FA. As mentioned before, fractions of the upgraded products (maltene, asphaltene, and coke) are measured by the solvent extraction method and the contribution of water in the reaction is quantified via AH_{rel} index through ATR analysis of the deuterated maltene.

In Fig. 5(a), comparison between the distribution of the products, i.e., maltene, asphaltene and coke according to the Eq. (1), as well as the contribution of water (AH_{rel}) after VR upgrading with iron (0) is depicted at different temperatures in SCW (left) and SCW + FA (right) conditions. While asphaltene content was reduced from 21 wt% in the

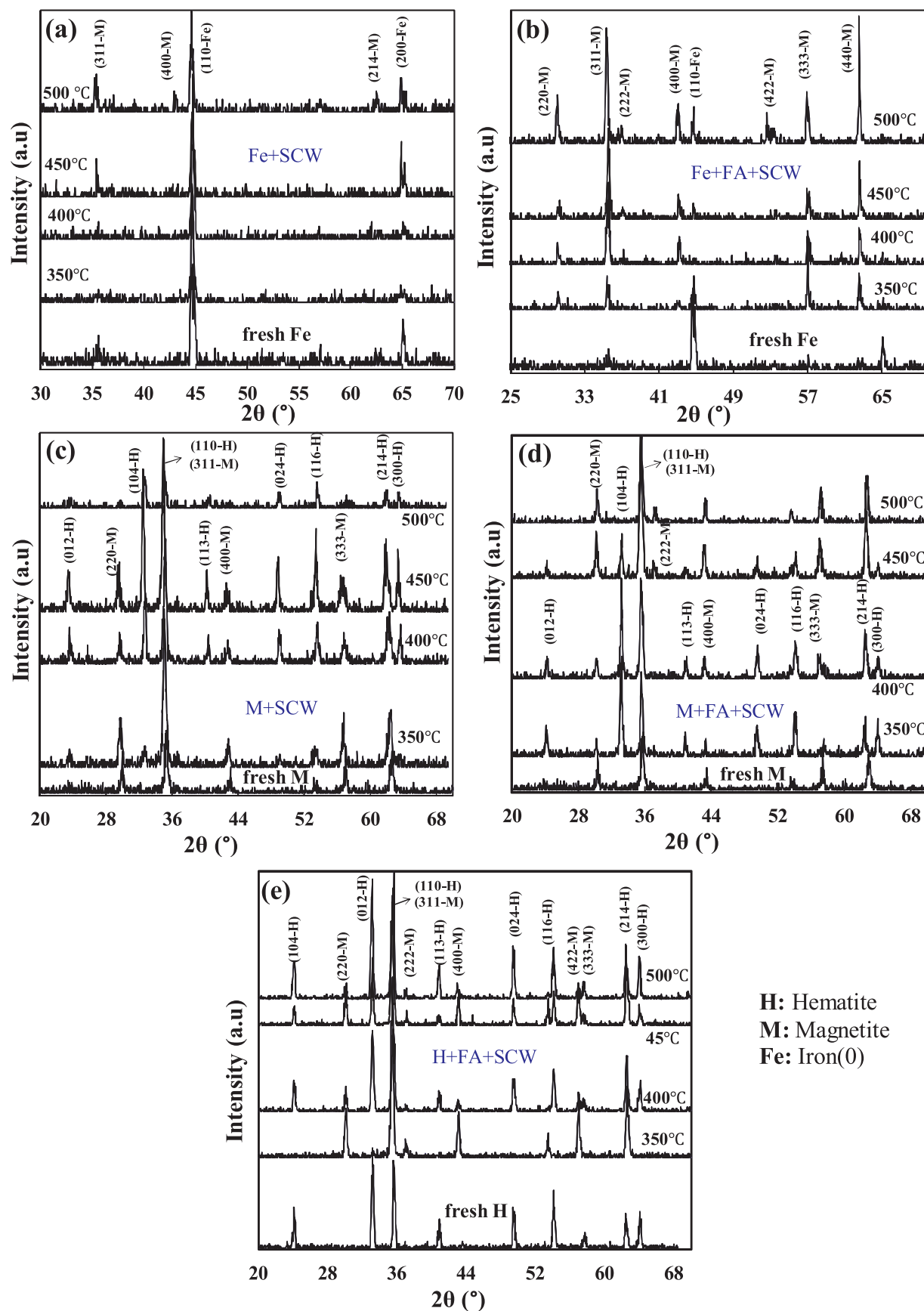


Fig. 2. XRD analysis of iron and iron oxides (magnetite and hematite) after treatment in SCW (a,c) and SCW + FA (b,d,e), respectively (Operational conditions: FA/H₂O = 1:2 v/v, catalyst/H₂O = 1/20 g/g).

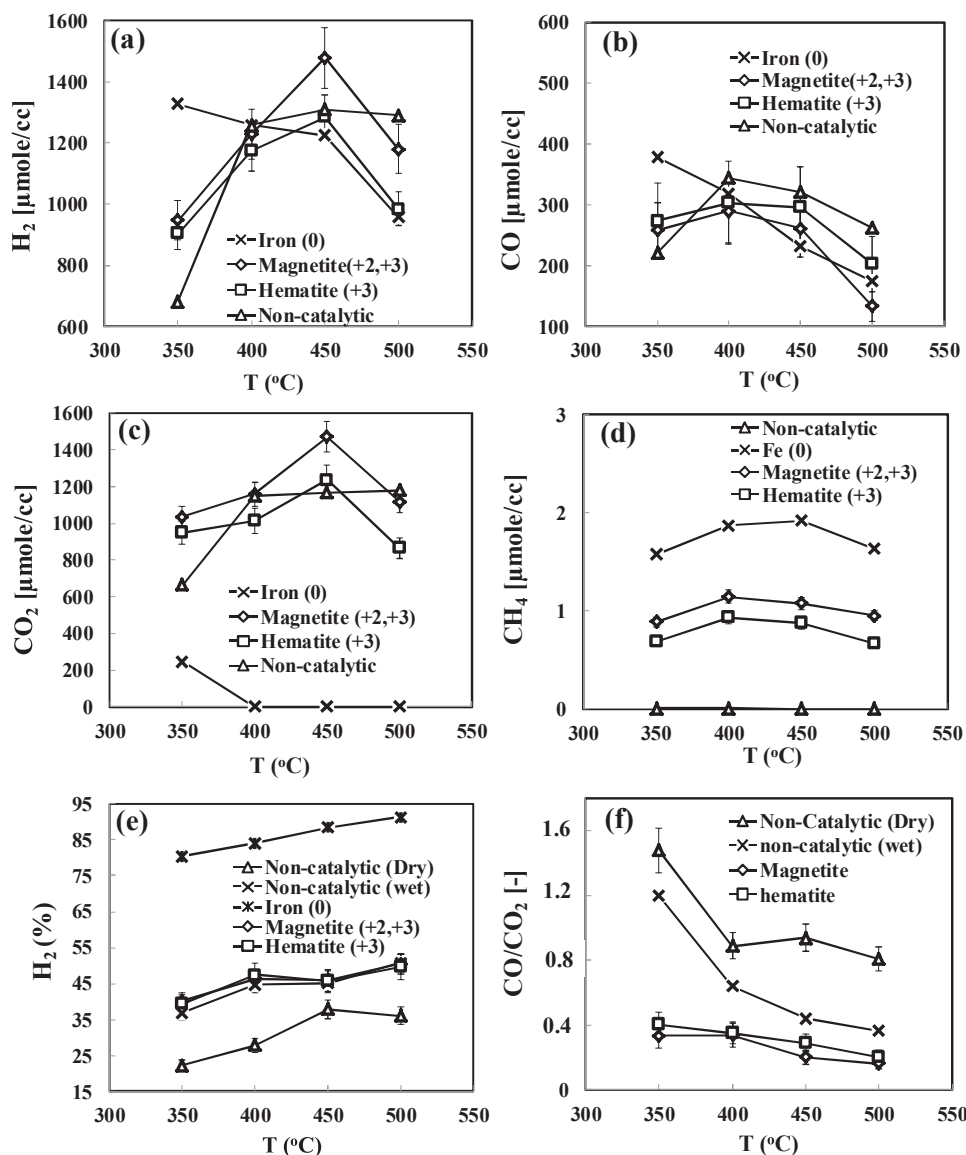


Fig. 3. GC-analysis of components from decomposition of FA in SCW (Operational conditions: FA/H₂O = 1:2 v/v, catalyst/H₂O = 1/20 g/g).

feedstock to topmost 12 wt% during upgrading in the absence and presence of FA, the coke formation was nearly in the same order (~20 wt%), indicating asphaltene to be easily transformed into coke. Since oxidative reactions take place over catalyst surface, all mass transfer barriers should be removed in advance. This issue can be provided by modification in solubility of organic phase in SCW via increasing temperature. It is evident that the AH_{rel} is increased by the temperature in both cases, which demonstrate the positive effect of the temperature on the removal of the mass transfer barrier by decreasing Hansen solubility parameters (δ_H), as an index of the miscibility between two oil-water phases [40]. Thanks to this process, the better solvation and dispersion of the heavy oil in SCW have been deduced. Consequently, more sites for the interaction between the cracked fragments and the active hydrogen from the WGS have been provided by the temperature. This can lead to the many other positive effects, for instance enhancement in the reactivity of the feedstock and shift in the thermodynamic equilibrium as well. However, they cannot be examined easily due to the complexity of the used feedstock.

However, comparing the results of Fig. 5(a) with Fig. 2(a,b), it is revealed that Fe⁰ is ineffective in providing demanded oxygen for cracking heavy constituents and they easily lead to the formation of coke.

In the presence of magnetite, however, the contribution of water is increased considerably in both cases (Fig. 5b) with the highest degree of AH_{rel} = 37%, maltene fraction, as well as the lowest asphaltene fraction (1.9 wt%) at 450 °C with FA, whereas, the amount of coke remains still significant. Compared to the heavy oil upgrading in the presence of Fe⁰, the lower fraction of coke, can be attributed to the active hydrogen produced by decomposition of water in the presence of magnetite. The contribution of water in the absence of formic acid is also considerable, and demonstrates the role of magnetite as a catalyst of the WGS reaction, which leads to the active hydrogen from water.

Compared to magnetite, the contribution of water is decreased in the presence of hematite, however, at 450 °C, the amount of the created coke in the absence and presence of FA decreased considerably, which can certify the importance of oxygen (oxygen in the lattice of iron oxide) on the decomposition of the heavy fragments and asphaltene (Fig. 5c). The temperature parameter demonstrates the importance of the phase behavior of SCW + VR system in the distribution of the product fragments: from 400 °C to 450 °C coke is suppressed because of the higher solvation and depression effect, while an increase in the temperature from 450 °C to 500 °C has a negative effect, since the pressure accelerates condensation of the poly-aromatics to asphaltene and coke. It is noteworthy that, due to the upgrading of the batch

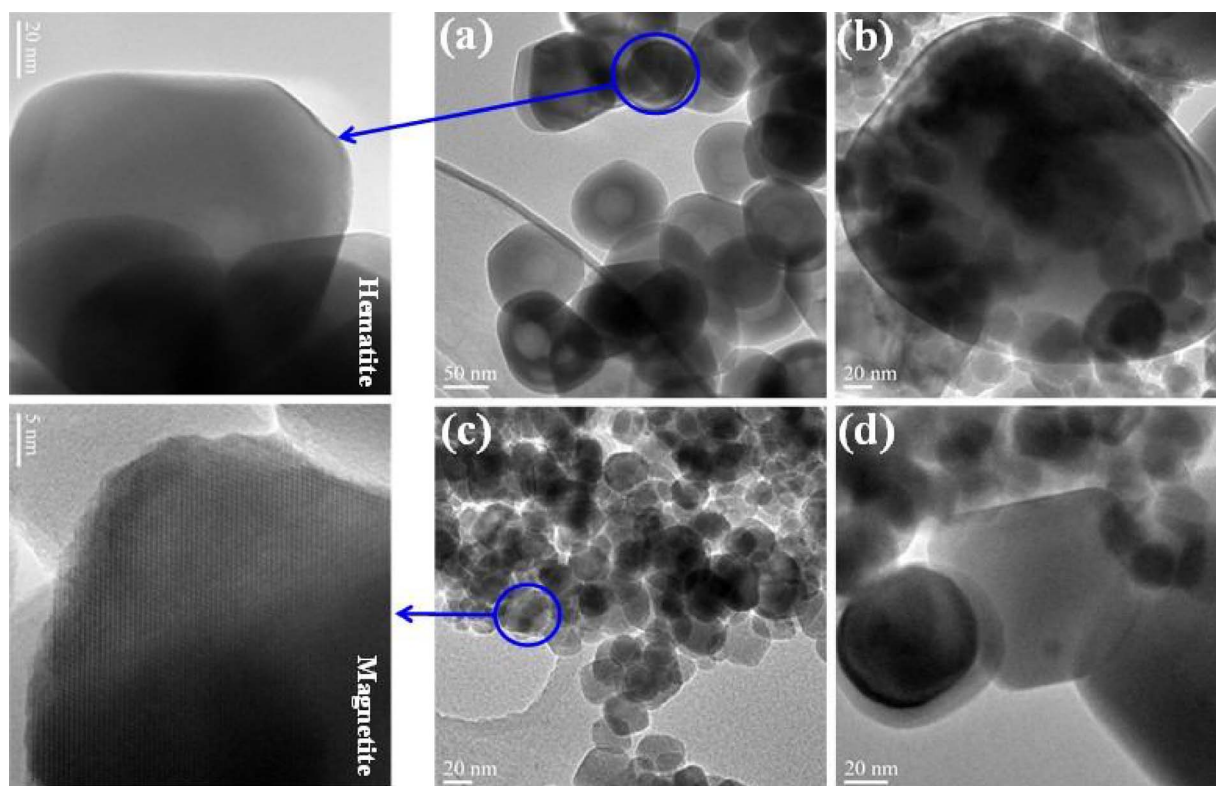


Fig. 4. Transmitting electron microscopy (TEM) of fresh (a,c) and used iron oxide (b,d) after treatment in SCW + FA.

system in the constant water density (0.2 g/ml), the increase of pressure is crucial from 450 °C (35MPa) to 500 °C (45MPa), while the change in Hansen solubility parameter is not considerable (δ_H (450 °C) = 8.5 compared to δ_H (500 °C) = 8.2 at constant ρ) [41]. It means that the miscibility status between the oil and SCW does not change significantly, but the raising pressure leads to the higher coke formation.

To take a more comprehensive view of the reaction environment, the fraction distributions of the upgraded oil as well as the contribution of water (AH_{rel}) in SCW condition and various agents (FA, hematite, magnetite) have been studied at 450 °C. As illustrated in Fig. 5, 450 °C and 1 h time are the optimal reaction conditions for VR upgrading to produce the highest total amounts of maltene with much less coke than that of observed in other temperatures. Fig. 6(a) and (b) shows the results of product distribution, AH_{rel} degree, heteroatom removal and H/C ratio, depending on upgrading medium, respectively. It is evident that in the absence of the active hydrogen and oxygen source, i.e., VR + SCW system, some parts of maltene will transform into the asphaltene and ultimately to the coke (maltene \rightarrow asphaltene \rightarrow coke). This procedure shows that the heavy oil cracking path in the SCW is similar to the neat pyrolysis system, which is processed via the free radical mechanism. In the presence of FA, as a source of active hydrogen, i.e., VR + FA + SCW system, the hydrogenation of light fragments (maltene) occurs more easily due to the better solvation in SCW, which is in sharp contrast to the oil-rich phase (asphaltene). As a result, the formation of coke via the condensation of asphaltene is crucial. Moreover, AH_{rel} is high enough (see Fig. 6a) to indicate that the active hydrogen from the SCW path has a significant effect on the saturation of maltene. Consequently, we just observe the conversion of asphaltene to coke (asphaltene \rightarrow coke) as the main process, compared to SCW pyrolysis system (SCW + VR).

The oxidative cracking of the oil-rich phase in the presence of hematite in the VR + SCW system and extraction of the cracked fragments to the water-rich phase by SCW leads to the less coke formation (maltene \leftarrow asphaltene \rightarrow coke). On the other hand, more coke is formed in the presence of magnetite compared to hematite, due to the insufficient

oxygen needed to crack the heavy components. Although AH_{rel} is comparable in both cases, due to the lack of sufficient hydrogen, some parts of maltene tend toward the asphaltene formation. This issue demonstrates the importance of the oxygen for transformation of the heavy constituents into the lighter fragments.

By introducing FA to the upgrading system in the presence of hematite, compared to magnetite, less coke with a higher degree of asphaltene is observed once again. AH_{rel} increases significantly in the presence of magnetite (Fig. 6a), which suggests that the oxygen can influence the transformation of asphaltene to the lighter fragments, while the active hydrogen helps the saturation of the light fragments. It means that the combination of FA and iron oxide (in higher oxidation state) is a proper candidate for achieving a higher degree of maltene with the less coke (asphaltene \rightarrow coke).

Since this paper emphasizes the study on the effect of water through isotopic labelling, one may ask the D incorporation to the product via H/D ionic exchange rather than through the reaction itself. VR + SCW reaction system in absence of FA and catalyst as a base experiment ($AH_{rel} \sim 7\%$), would help to answer the question. To better illustrate, it is worth mentioning that due to the ionic nature of isotope exchange, the probability of H/D exchange between supercritical D_2O and hydrocarbon would be low. In the hydrothermal medium at low temperatures, the exchange process takes many hours and days to reach equilibrium due to the thermodynamic restrictions [42]. In SCW condition, the exchange is even worth since the ionic nature of water goes toward non-ionic, which means that in these conditions water exhibits non-polar properties. Hence the degree of H/D exchange is expected to be suppressed, significantly. The study of deuteration of benzene in our recent investigation proves this claim. In that study [43], the exchange degree in the absence of suitable catalyst (i.e., NaOD) was impossible in low time duration (1 h). Further, the degree of deuteration of organic compounds via H/D exchange decreases from aromatics to aliphatics (aromatics $>$ alkenes $>$ alkanes), in contradiction to the results of current study in which deuterated aliphatic compounds are predominant. Nevertheless, with such degree of heteroatoms in VR feed,

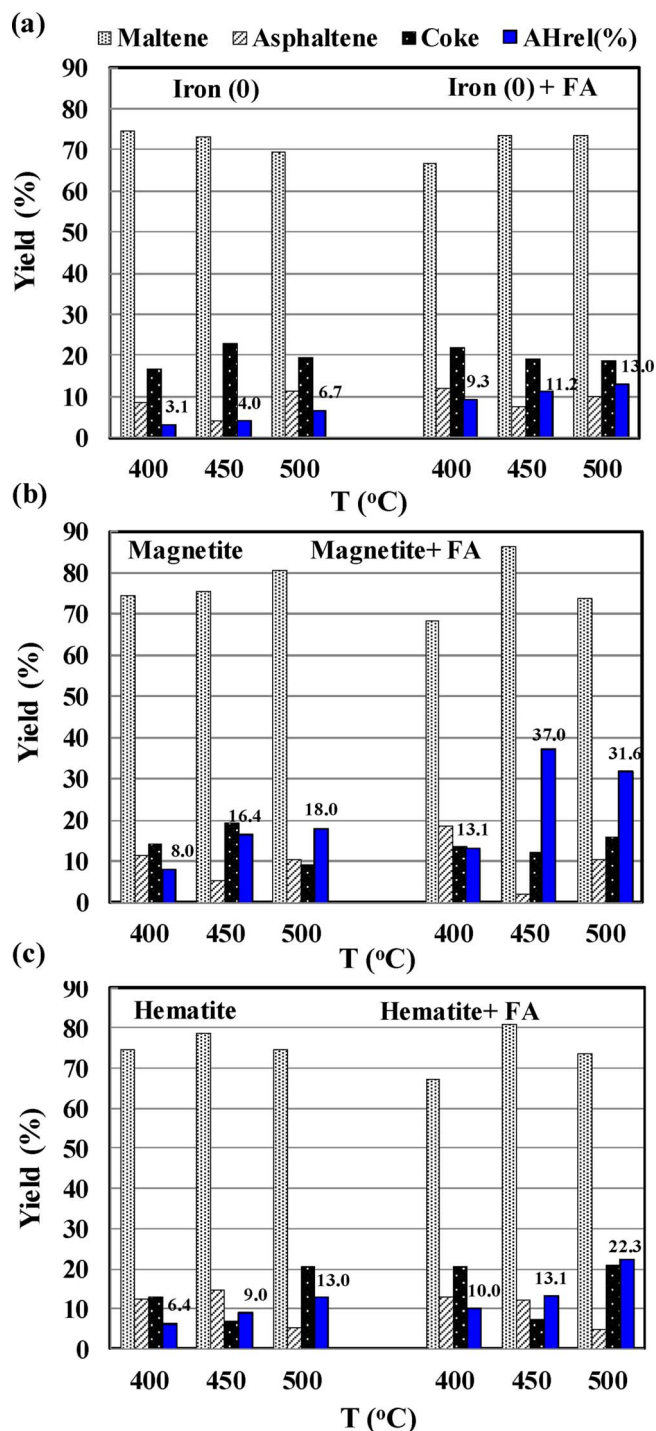


Fig. 5. Weight distribution of upgraded oil after treatment in SCW (left) and SCW + FA (right). (Operational conditions: FA/D₂O = 1:2 v/v, catalyst/D₂O = 1/20 g/g, VR/D₂O = 1/2 g/g).

the carbons nearby heteroatoms are susceptible to participate in the reforming chemistry in SCW without catalyst. Consequently, the contribution of water in the absence of catalyst, in VR + SCW upgrading system, through the reaction cannot be ignored.

The elemental analysis (CHNOS) of the upgraded oil (maltene + Asphaltene) obtained from above-mentioned upgrading system is shown in Fig. 6(b). Compared with the results of Fig. 6(a), high hydrogen to carbon ratio (H/C = 1.71) of upgraded oil resulted from VR + SCW system can be attributed to the effective hydrogenation from condensation of polyaromatics with considerable formation of

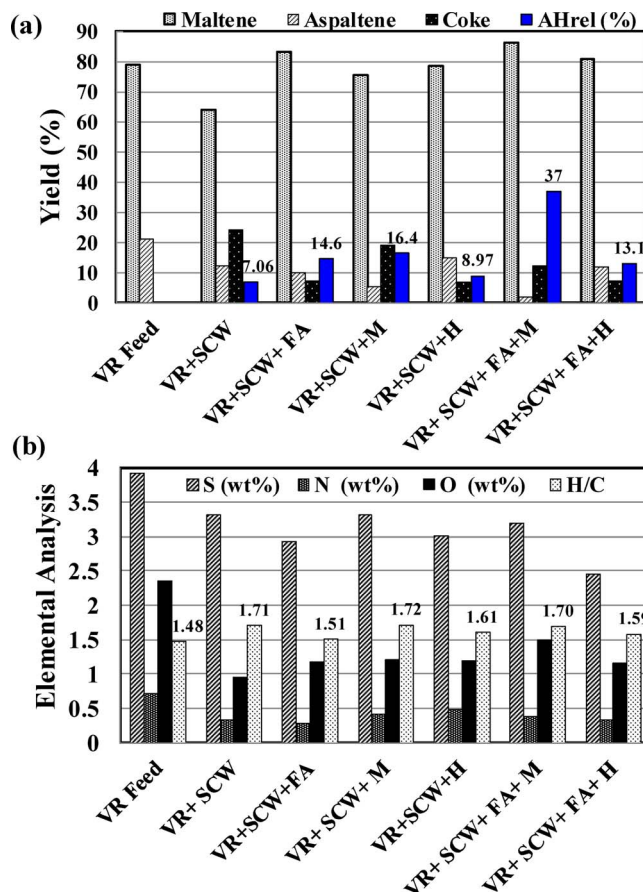


Fig. 6. (a) Weight distribution of upgraded oil (maltene + Asphaltene) as well as contribution of water in hydrogenation (AH_{rel}) of oil, and (b) Removal of hetero atoms and H/C ratio of upgraded oil in different medium (Operational conditions: T = 450 °C, FA/D₂O = 1:2 v/v, catalyst/D₂O = 1/20 g/g, VR/D₂O = 1/2 g/g, M: Magnetite, H: Hematite).

coke (coke = 24 wt%). Similar amount (H/C = 1.70) was obtained from VR + SCW + FA + magnetite system with low coke (12.10 wt%), representing better hydrogenation of oil in the presence of magnetite and FA through active hydrogen created from water (AH_{rel} = 37%). The highest amount of H/C ratio belongs to the VR + SCW + magnetite upgrading system (H/C = 1.72) with the amount of coke (19.24 wt%) between two above-mentioned VR + SCW and VR + SCW + FA + magnetite systems, indicating the role of water and hydrocarbon as hydrogen donors via WGS (AH_{rel} = 16.4%) and polycyclic aromatic hydrocarbons (PAH) condensation, respectively.

Further, the removal of the sulfur heteroatom in the VR + SCW + FA + hematite system was considerably higher than other upgrading systems, which shows that in the presence of iron oxide, oxidative desulfurization (ODS) is more effective than hydrodesulfurization (HDS). However, the low sensitivity of other heteroatoms (nitrogen and oxygen) to catalyst indicates that catalyst type has the greatest influence on the fraction of N and O-containing compounds remained in the treated oil of this study. Thus, there is a need of catalyst screening studies for HDN and HDO in SCW, so that effective catalysts rather than iron oxide could be identified. Several studies on removal of such compounds (especially nitrogen in heterocyclic compounds) in real feed and model compounds showed that their removal in the lone SCW medium (no catalyst) is apparently difficult [26–28]. It means that the removal of nitrogen and oxygen in the absence of catalyst (i.e., VR + SCW and VR + SCW + FA systems in Fig. 6) can be related to their presence in PAH compounds which are removed from the system by the coke formation.

Fig. 7 shows the thermogravimetric analysis (TGA) of upgraded oil

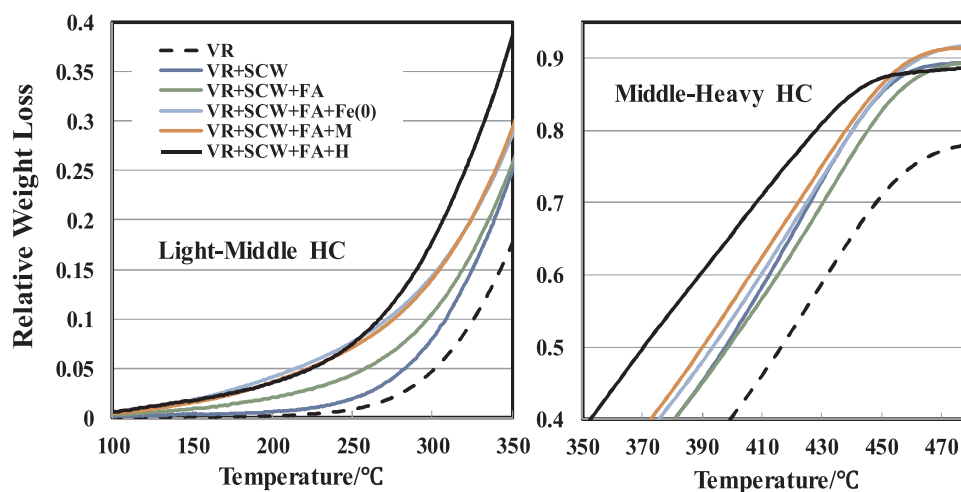


Fig. 7. Thermogravimetric analysis of (TGA) oil feed and upgraded oil product at various environment (Operational conditions: $T = 450\text{ }^{\circ}\text{C}$, $\text{FA}/\text{D}_2\text{O} = 1:2\text{ v/v}$, catalyst/ $\text{D}_2\text{O} = 1/20\text{ g/g}$, $\text{VR}/\text{D}_2\text{O} = 1/2\text{ g/g}$, M: Magnetite, H: Hematite).

which demonstrates the temperature when the fraction is volatilized and/or decomposed thermally. Through relating the results to the TGA analysis of the upgraded oil, it can be seen that by increasing the temperature, the distributions of the upgraded oil that result from the VR + SCW and VR + SCW + FA systems meet each other (see Fig. 7 right), and demonstrates that FA effectively acts as a hydrogen donor of the lighter fragments with the volatility lower than $350\text{ }^{\circ}\text{C}$. Additionally, for all types of iron oxide, the distribution of the components for the upgraded oil in the presence of FA is nearly the same for the light components ($T < 260\text{ }^{\circ}\text{C}$), while the trend in the case of VR + SCW + FA + hematite system diverges after $T = 260\text{ }^{\circ}\text{C}$. Once again, this issue confirms that the hematite type iron oxide with a higher degree of oxygen lattice is active for the heavy constituents, while magnetite can act better for the hydrogenation of the lighter fragments. Considering the three main criteria of (1) the higher recovery of upgraded oil (2) the less coke, and (3) the higher removal degree of heteroatoms, the performance of the upgrading system can be categorized as the following order:

SCW + FA + hematite > SCW + FA + magnetite >
SCW + FA + Fe° > SCW + FA > SCW

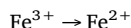
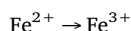
3.3. Effect of water pressure on the catalyst activity

Although the in-situ study of the water pressure on the redox property of the iron oxide is impossible, the ex-situ analysis of the spent catalyst can provide relevant information. Fig. 8 shows the XRD patterns of the spent catalysts in the VR + SCW + FA + M system under low and high pressure (density) conditions. According to this Fig. 8, after the reaction at subcritical pressure (14 MPa), the pattern shows the peaks corresponding to magnetite (Fe_3O_4), and almost no peak corresponding to hematite has been observed. In contrast, under supercritical condition ($P_w = 35\text{ MPa}$), the main peak related to hematite is appeared, which indicates that the FeO_x in the catalyst has been oxidized from magnetite to hematite ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$), preferable condition for oxidative heavy oil upgrading. The increase of water pressure provides an increased access to the iron active site with the higher rate of water splitting. This would be more considerable when the limitation of the WGS reaction on iron oxide in the atmospheric condition is examined. Total agreement has been made on the dissociative (redox) nature of this reaction in the steam atmosphere with regard to the two-rate determining (limiting) steps [44]:

- (1) Diffusion of CO and H_2O from gas-phase to the catalyst surface. Due to an increase in the solubility and diffusivity of the reactant (CO) and

the products (H_2 , CO_2) in SCW, the suppression in the thickness of the film layer over the catalyst surface increases the mass transfer rate as expected.

- (2) Reaction between the absorbed components over the catalyst surface (Langmuir–Hinshelwood mechanism). According to the proposed mechanism, first, water decomposes to the hydrogen and the absorbed oxygen on the catalyst surface and it is followed by CO_2 production from CO and absorbed oxygen:



Contrary to the hematite crystals, with closely packed oxygen lattice with Fe^{3+} cations occupying octahedral sites, magnetite has an inverse spinel structure with oxygen ions forming a face-centred cubic closely packed structure [44]. The inverse spinel structure formula (Fe^{3+}) $[\text{Fe}^{2+}, \text{Fe}^{3+}]_4\text{O}_4$ can describe the magnetite with Fe occupancy where the parentheses () and brackets [] denote cations at tetrahedral and octahedral lattice sites, respectively. Contrary to the steam, SCW can provide higher water to H_2 , CO_2 and CO ratios, the equilibrium between the Fe^{2+} and Fe^{3+} ions in octahedral sites is expected to change toward higher oxidation state, while the reactants (hydrocarbon, CO , H_2) try to decrease the oxidation state. This situation probably provides rapid electron exchange between Fe^{3+} and Fe^{2+} ion, which is responsible for the higher WGS activity. In case of the substantial contribution of SCW to the redox property of the iron oxide, the modification in the heavy oil conversion to the lighter products with a suppression in the coke formation is anticipated (see AH_{rel} in Fig. 8). It is noteworthy that the magnetite, which is an active phase for WGS reaction as a catalyst, occurs in a temperature between $350\text{--}450\text{ }^{\circ}\text{C}$, which is an appropriate temperature range for the heavy oil upgrading [40]. Since the WGS is reversible, the rate of WGS is strongly influenced by the products (CO_2 , H_2); therefore, more solubility of gases in SCW can forward this reaction to the higher H_2 production than the steam atmosphere. Beside the solvation effect, the mass transfer on the catalyst surface (diffusion effect) can also accelerate the WGS rate in the SCW condition toward a higher active hydrogen, which in turn leads to the production of higher light oil with the less coke (compare product distribution in Fig. 8).

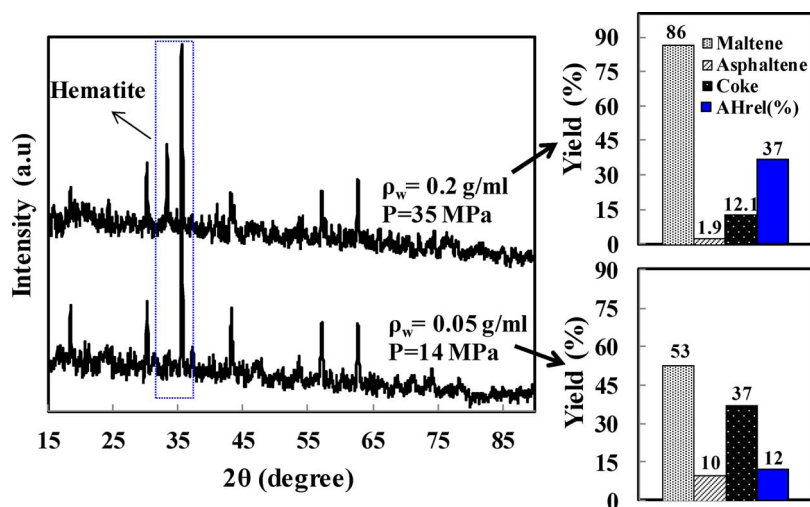


Fig. 8. XRD analysis of spent magnetite shows the appearance of hematite related peak by increasing water density. (Operational conditions: $T = 450\text{ }^{\circ}\text{C}$, $\text{FA}/\text{D}_2\text{O} = 1:2\text{ v/v}$, magnetite/ $\text{D}_2\text{O} = 1/20\text{ g/g}$, $\text{VR}/\text{D}_2\text{O} = 1/2\text{ g/g}$).

3.4. Possible path of AH from SCW in the presence of iron oxide and FA

As it has been mentioned before, the physical effects of SCW (solvation and dispersion) have been studied extensively during the upgrading of heavy oil [33,40,45]. Hence, it is expected that by removing the mass transfer limitation in SCW, the catalyst performance accelerates effectively. Fig. 9 depicts the proposed path of the heavy oil upgrading in SCW via replacing H_2O with D_2O (isotope labeling technique) in the presence of the iron oxide and FA. Under the high-pressure conditions, since the consumption/regeneration reactions were cycled effectively, the catalyst structure was remained as hematite, as shown in Fig. 8, and that is favorable for the oxidative cracking. By rejecting carbon from this site through the lattice oxygen, the iron oxide reduces ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$) following the splitting of water over the

converted iron oxide, hence recompensing its initial state ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$). This issue leads to the generation of AH for saturating the broken bonds of non-saturated compounds. Due to the capability of SCW to extract the light oil compounds, now the lighter products are ready to be diffused to water rich phase. This phenomenon will continue until depletion of alkyl chains from the poly-nuclear aromatic chains.

The stability study of the catalyst and the coke deposition has been investigated in detail by the same authors elsewhere [29,30,46]. In that study, they proposed a SiO_2 -supported $\alpha\text{-Fe}_2\text{O}_3$ to approach higher stability compared with the same free $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles.

4. Conclusion

Due to the increasing attention of the refineries to the innovative

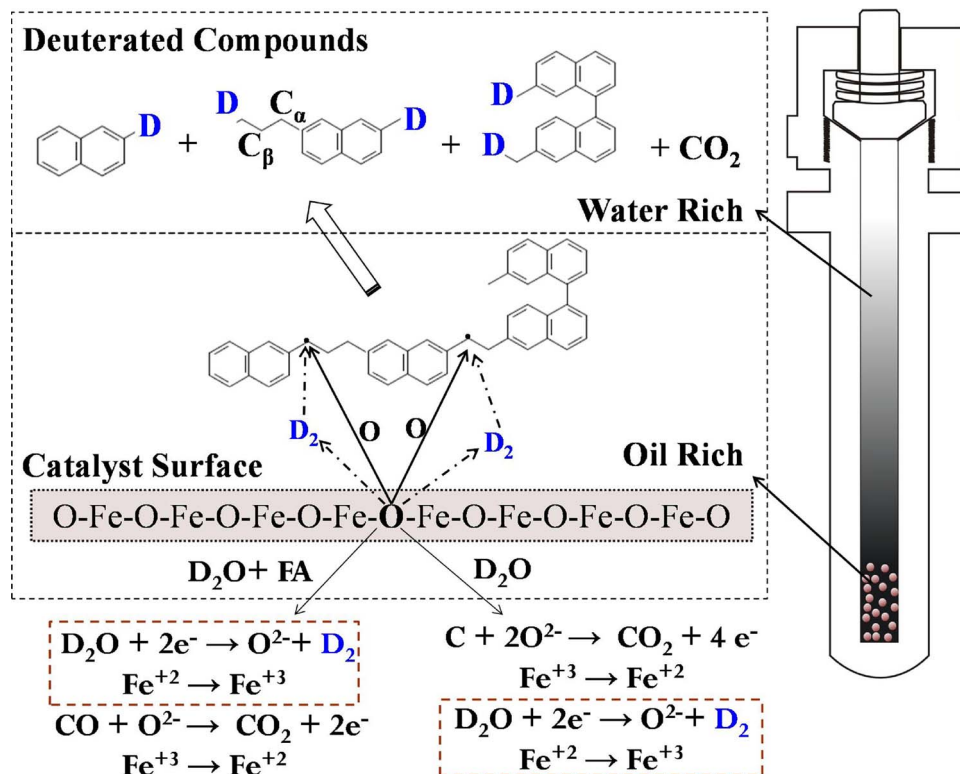


Fig. 9. Possible path of heavy oil catalytic upgrading in SCW medium in the presence of iron oxide and FA.

techniques of heavy oil upgrading with environmental advantages, the present paper is focused on the VR upgrading in SCW with iron oxide nanoparticles as catalyst. The process was studied by catalytic cracking of vacuum residue (VR) in the presence of the different types of iron oxides, and FA solution in SCW condition. It is concluded that the higher oxidation state of iron oxide can lead to the higher yield and lighter liquid product with the less coke formation. The isotopic analysis of the deuterated oil indicated that magnetite would accelerate in-situ hydrogen production from SC water, to be able to react with light cracked fragments, while the released oxygen would be more suitable for oxidation of heavy constituents to the light fragments with higher heteroatom removal efficiency. Against atmospheric steam, SCW can recompense the converted iron to a higher oxidation state with the modification in the redox cycle ($\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$) by avoiding deactivation of the catalyst from depletion of the lattice oxygen.

The outcomes of this research could not only create an innovative route for more profitable FA utilization than the external hydrogen from the natural gas steam reforming, but also can be beneficial to the heavy oil upgrading with effective heteroatoms removal in a more economical and environmental friendly way. However, development of new engineering solutions for proposed upgrading process, particularly recycling the gas products, seems inevitable in order to improve the process economic as well as decrease the impact of CO_2 as greenhouse gas. One of the solutions for CO_2 removal would be recycling the released gas to the dry reforming plants of methane to produce more synthesis gas.

Acknowledgements

The authors would like to thank the Institute for Solid State Physics (ISSP), the University of Tokyo for providing XRD and TEM analyses.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.02.030>.

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